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THIN-FILM EVAPORATION AS A PRETREATMENT TECHNIQUE FOR REMOVING VOLATILE ORGANICS FROM PETROLEUM REFINERY WASTES

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ABSTRACT

Oily wastes from petroleum refineries can result in air emissions during the land treatment of these wastes. A pilot-scale thin film evaporator (TFE) was used to remove volatile organics (VO) from refinery tank bottom sludge. Different TFE operating parameters were utilized to determine optimum process operating conditions and the percent removal of specific VO compounds was measured. Removal efficiencies of up to 99.9% were obtained, resulting in a 95% reduction in VO emissions from a land treatment test plot.

INTRODUCTION

Many industries, including the petroleum industry, use land treatment to dispose of oily wastes. In land treatment of petroleum sludges, the oily wastes are mixed into the upper layer of soils that contain active microorganisms. Over a period of time, these microorganisms degrade the organics. During waste application and for a short time after, volatile organics (VO) will diffuse into the air relatively rapidly. If the volatile fraction is removed from the waste prior to disposal, the resulting migration of organics into the air can be greatly reduced.

Under the sponsorship of the EPA, thin-film evaporation, a potential pretreatment process for removing VO from petroleum refinery wastes prior to land treatment, was evaluated by the Research Triangle Institute (RTI).

LAND TREATMENT OF REFINERY WASTES

In land treatment of refinery wastes, the waste is either spread, injected, or sprayed onto the ground. The waste, a mixture of solids, water, and organics, and soil are then tilled to bring soil microorganisms into contact with the organics. Generally wastes are mixed with the soil to a depth of 6 inches to 1 foot. This layer, or zone of incorporation, is where most of the biodegradation takes place. Once acclimated to the specific waste type, the soil microorganisms break down the organics into lighter weight organics, water, and carbon dioxide. Periodic fertilization and tilling are sometimes necessary to provide the oxygen and nutrients required for degradation. The proper pH in the soil/waste mixture is also important to allow degradation and to prevent metals, such as lead and chromium from leaching into the ground water (1).

Land treatment has been used in the U.S. as a method for treatment and disposal of refinery wastes since 1954. As of 1983 it was estimated that at least one third of all U.S. refineries used this technology for some of its wastes (2). Little data exists, however, regarding air emissions from these sites (3).

THE THIN-FILM EVAPORATION PROCESS

Agitated thin-film evaporators (TFEs) are designed to spread a thin layer of viscous liquids or sludges on one side of a metallic surface with heat supplied to the other side. This promotes the transfer of heat to the material while simultaneously exposing a large surface for evaporation of

volatile compounds. Heat can be supplied by either steam or heated oil; heated oils are used to heat the waste to temperatures higher than can be achieved with saturated steam. Volatile constituents separate from the feed liquid or sludge, producing a vapor stream of volatiles and leaving a treated waste which flows out of the bottom of the evaporator. Evaporated volatiles can be condensed and recovered.

The unique feature of this equipment is not the thin film itself (falling- and rising-film evaporators use thin liquid layers), but rather the mechanical agitator device for producing and agitating the film. This mechanical agitator permits the processing of high-viscosity liquids and sludges with suspended solids. The agitation at the heat transfer surface not only promotes heat transfer but also maintains precipitated or crystallized solids in manageable suspension without fouling the heat transfer surface.

With typical tip speeds of 900 to 1,200 cm/s (30 to 40 ft/s), centrifugal forces distribute the feed as a thin film on the heated cylinder wall, and the wave action produced by the rotating blades provides rapid mixing and frequent surface regeneration of the thin liquid layer on the transfer surface. A typical vertical thin-film evaporator is illustrated in Figure 1.

The use of TFEs was investigated to determine if VO can be removed and recovered from waste petroleum sludges prior to land treatment. This would reduce the amount of VO available for release to the atmosphere during land treatment of the sludges. The VO would be recovered as an organic condensate and recycled to petroleum refineries as product. In addition to VO removal, the process can also be operated to remove water and low boiling oils from sludges, thus reducing sludge volume while recovering oil from sludges prior to disposal.

PILOT-SCALE FACILITY AND TEST

Equipment

The tests were conducted at the pilot facility of a TFE manufacturer in September, 1986. Samples of tank bottoms sludge were obtained from an oil refinery, tested in the equipment, and then returned to the refinery for normal disposal. Because of regulatory constraints, only nonhazardous refinery wastes (as defined by RCRA) were tested. These wastes were chosen because they are typical of oily wastes with relatively high volatile organic content that are land treated at petroleum refineries.

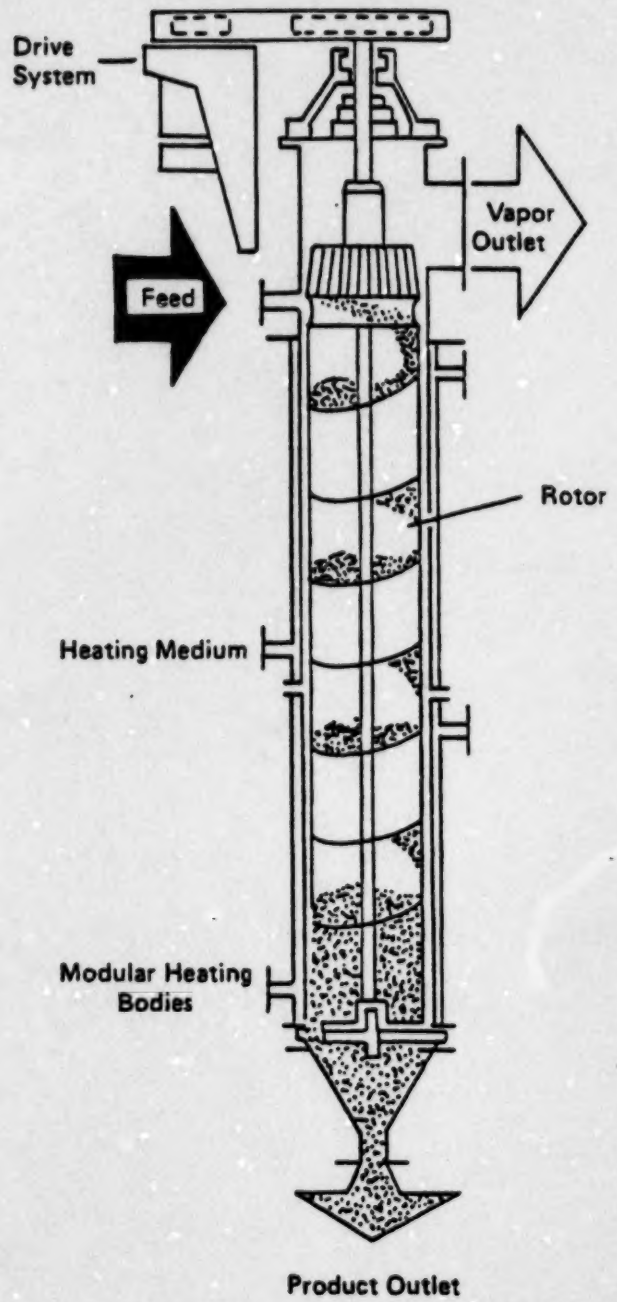

Figure 1. Typical vertical thin-film evaporator.

Figure 2 shows the equipment used in the pilot-scale tests. A 100-gal feed tank was agitated with both an axial mixer and continuous recirculation of the feed liquid through a centrifugal pump. A positive displacement pump was used to pump the feed sludge through the preheater and into the top of the TFE. There, the sludge was continuously spread over the heated surface of the TFE. Unevaporated material flowed down through the TFE to a collection pot at the base. Evaporating materials passed through an empty demister and a condenser. Condensate flowed from the condenser and was collected directly into liquid sample jars or a flask used for measuring condensate volumes. Any uncondensed vapors flowed from the condenser through a wet testmeter for flow measurement.

Operation

A matrix showing operating conditions and run numbers for each of the 22 tests is illustrated in Table I. Two waste types, three temperatures, and three feed rates were selected to evaluate the TFE over its normal range of operation and to demonstrate the removal of VO from the feed sludge. The TFE was evaluated using results from Tests 1 through 18. Tests 19 through 22 were conducted to demonstrate the operation of the TFE using a second waste material and were not extensively sampled or analyzed during the project. Three runs (11, 17, and 18) were performed under vacuum and were used to determine the effect of this type of operation on VO removal. Runs 1 through 4, 12, and 13 were used as shakedown runs. These runs allowed practice samples to be taken and problems to be solved before the samples to be analyzed were taken.

Four of the tests (5, 7, 8, and 10) were selected for extensive sampling and analysis of process streams. These four runs allowed the process to be examined with both high and low feed rates and at both high and low heating temperatures. They represent the range of reasonable operating conditions for the TFE processing waste sludges for the removal of volatiles, water, and oils from the sludge.

Sampling and Analysis

Samples were taken to characterize the wastes and to determine the efficiency of the TFE process. Four process streams were sampled: feed, bottoms, condensate, and condenser vent gas.

Samples were analyzed onsite by RTI and offsite by contract laboratories. The onsite measurements performed by RTI were:

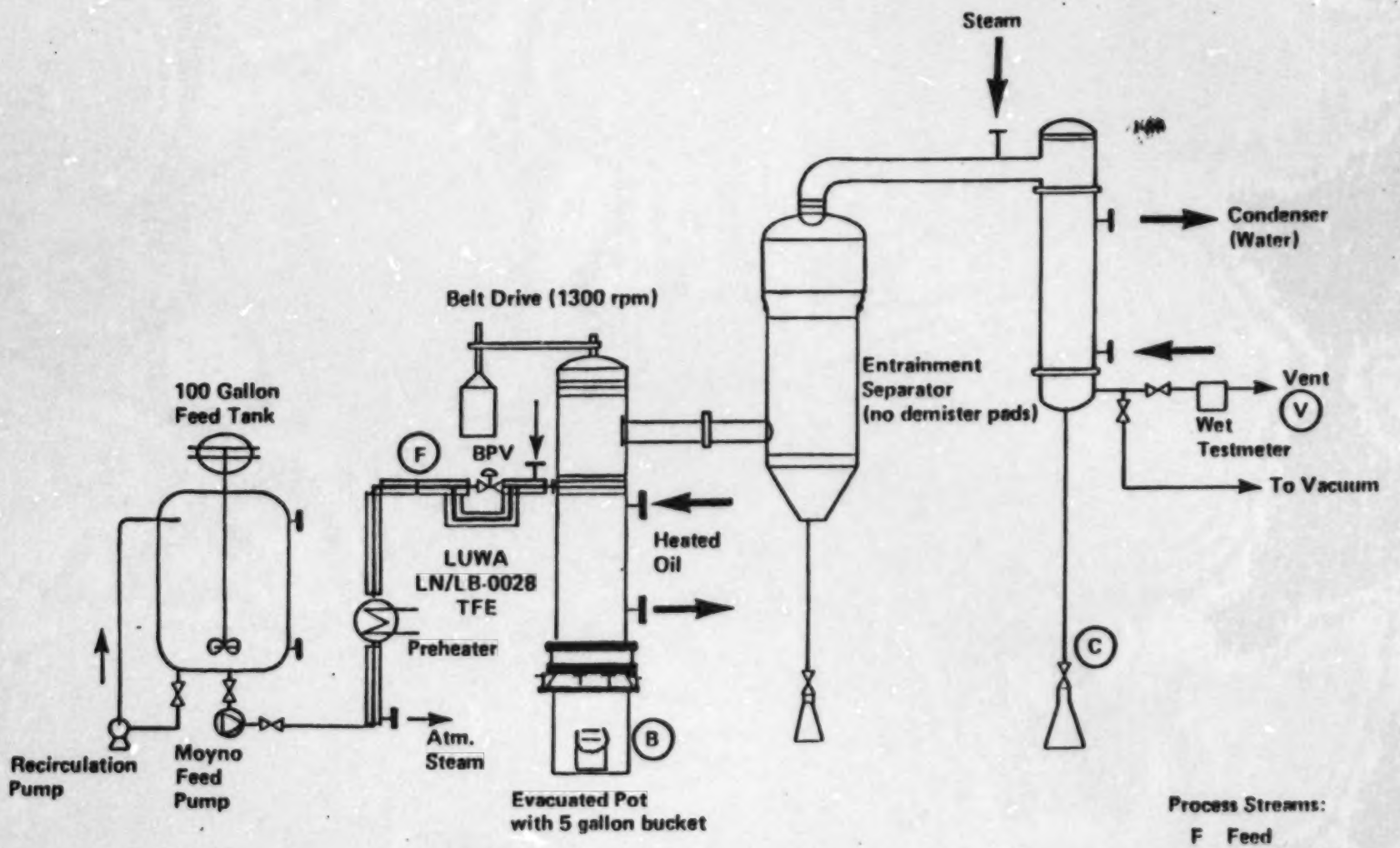

Figure 2. Configuration of test equipment.

Table I. TFE Test Conditions

Waste type	Run number	Flow rate (lb/h)	Temperature (°C)	Pressure
Emulsion tank sludge	1-4	-------- Equipment test --------		
	5	70	150	atm.
	6	100	150	atm.
	7	150	150	atm.
	8	70	310	atm.
	9	100	310	atm.
	10	150	310	atm.
	11	23	310	vac.
	12-13	-------- Equipment test --------		
	14	70	230	atm.
	15	100	230	atm.
	16	100	230	atm.
	17	57	150	vac.
	18	57	100	vac.
Oily tank bottoms	19	45	310	atm.
	20	80	310	atm.
	21	45	150	atm.
	22	80	150	atm.

(1) the analysis of headspace concentrations of VO from feed sludge and bottoms samples and (2) the measurement of vent gas flow rates and overall VO concentrations in the vent gas and bottoms collection pot. Two types of analyses for headspace concentrations of VO were employed. The first used a portable gas chromatograph (GC) to measure the VO concentrations in the sample bottle headspace. The second method used a calibrated total hydrocarbon analyzer (THCA).

The THCA was also used to measure concentrations of organics in the vent gas, feed tank headspace, and vapors above the bottoms when the sample pot was removed from the TFE.

Samples of the TFE feed, bottoms, and condensate from Runs 5, 7, 8, and 10 were analyzed by a contract laboratory for volatile and semivolatile organics; percent oil, solids, and water; and metals. The purpose of these analyses was to evaluate the process effectiveness on an individual component basis.

Land Treatment of TFE Bottoms

For thin-film evaporation to be a practical pretreatment process for land treated refinery wastes, the bottoms from the TFE must be land treatable. To evaluate this, the feed and bottoms from Runs 7 and 8 were tested using a pilot-scale land treatment apparatus (4). The purpose of these tests was to evaluate the volatilization and biodegradation when these wastes are land-treated and to determine the effect of thin-film evaporation on these mechanisms.

The pilot-scale land treatment apparatus consisted of a stainless steel trough, a clear acrylic dome, a blower, and an air filter. The bottom of the trough was slightly sloped with a valve at the low point to allow for leachate drainage. The apparatus had glove ports to allow waste application, soil tilling, watering, and sampling to be performed without introducing outside air. The conditions within the apparatus were carefully controlled to simulate an actual land treatment facility and to allow for an accurate evaluation of the fate of the applied materials.

RESULTS AND DISCUSSION

The feed rate and temperature of the TFE were varied over its normal range with no observed problems when operated at atmospheric pressure. There were however difficulties when it was operated under vacuum at 320 °C, as some carryover of feed into the condensate was observed. The condensate from the vacuum runs was a milky-white emulsion, which would require

additional treatment to separate the oils. All of the other runs resulted in a cleanly separating organic/aqueous condensate.

When the TFE was operated at the 150 °C, some of the water in the feed was evaporated along with most of the VO. As illustrated in Table II, the VO removals ranged between 99.5 and 99.6 percent at the low feed rate and decreased slightly when the feed rate was increased. The bottoms temperatures for these runs were 98 to 102 °C, indicating that water was still boiling from the bottoms as it exited the base of the TFE.

The removal efficiency for volatiles was greater when the TFE was operated at higher temperatures. The VO removals when the TFE was operated at 310 °C were 99.7 to 99.9 percent, with no clear trends relative to changes in feed rate. These runs removed essentially all of the water and VO from the feed sludge, along with much of the higher boiling oils. The amount of bottoms sludge produced ranged between 10 and 13 percent of the feed rate, substantially reducing the amount of material requiring disposal. This bottoms product was a relatively viscous, high solids content sludge, which was still pumpable.

The percent removal of selected semivolatile components from the refinery waste is given in Table III. As can be seen, the TFE was effective at removing some, but not all, of the semivolatiles. In fact, several of the less volatile components were concentrated in the TFE bottoms as indicated by the negative percent reductions. These high-boiling compounds were not volatilized at the operating conditions and were therefore concentrated in the reduced volume of bottoms.

A visual example of the effectiveness of the TFE is given in Figure 3. Shown are the chromatograms from the VO analysis performed on the feed and bottoms from Run 5 (5). The attenuations for the two analyses are similar, so the sizes of the peaks can be directly compared between the feed and bottoms. As seen in Figure 3, the organics up to the xylene boiling range are effectively removed. It is only at the end of the chromatogram, where semivolatiles such as naphthalene are detected, that constituents remain in significant concentration.

Another demonstration of the organic removal was in the gas chromatography analysis of the headspace gas over the feed and bottoms. As seen in Table IV, the organics in the vapor above the samples were reduced on the order of 99 percent or more, depending on the conditions. This suggests that the potential emission of organic pollutants into the atmosphere during land treatment has been reduced substantially.

Table II. TFE VO Removal for Selected Compounds

Run No.	Operating Conditions		Reduction in concentrations from feed (%)[a]			
	Temp. (°C)	Flow rate (lb/hr)	Benzene	Toluene	Ethyl-benzene	m-Xylene
5	150	70	99.6	99.6	99.5	99.5
7	150	150	99.7	99.8	98.8	98.6
8	310	70	99.7	99.8	99.7	99.7
10	310	150	99.8	99.9	99.8	99.8

[a]Based on laboratory GC/MS analyses.

Table III. TFE Semivolatile Removal for Selected Compounds

Run No.	Operating Conditions		Reduction in concentrations from feed (%)[a]			
	Temp. (°C)	Flow rate (lb/hr)	Naph-thalene	2-Methyl-naph-thalene	Fluorene	Chrysene
5	150	70	79.1	59.5	53.2	46.9
7	150	150	32.0	16.5	36.8	0
8	310	70	94.0	84.8	27.5	-118.8
10	310	150	96.9	87.5	0	-168.8

[a]Based on laboratory GC/MS analyses.

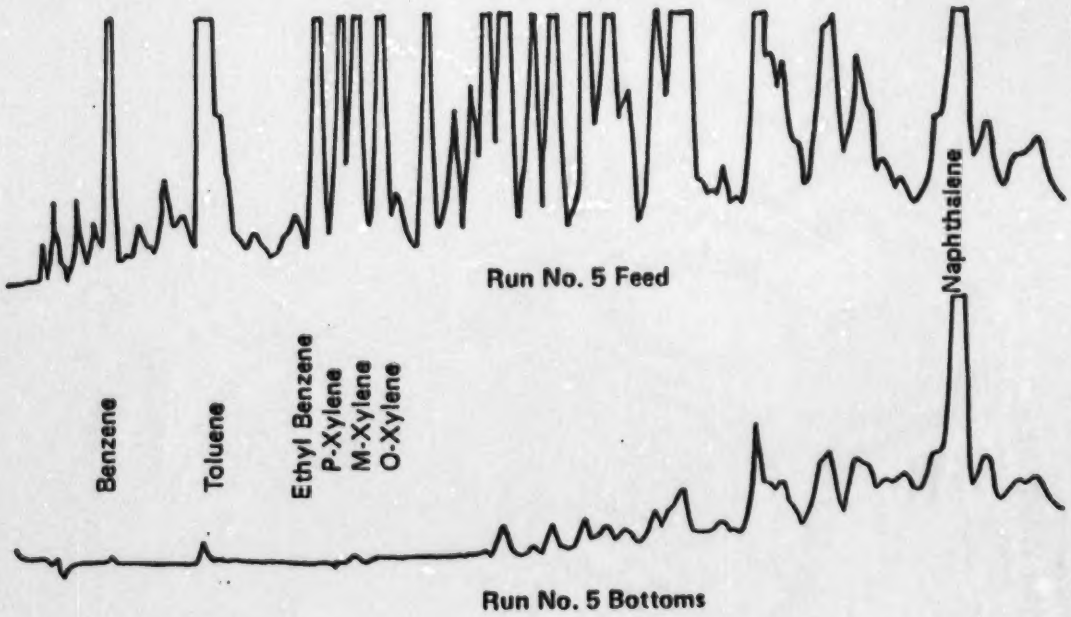

Figure 3. Effectiveness of TFE at removing VOCs from tested waste.

Table IV. Summary of GC Headspace Analysis

Run No.	Operating Conditions: Temp. (°C)	Operating Conditions: Flow rate (lb/hr)	Reduction in concentrations from feed (%)[a]: Benzene	Toluene	2-Methyl-butene	Pentane
5	150	70	99.9	99.1	99.9	99.9
7	150	150	99.9	99.5	99.9	99.9
8	310	70	99.7	99.6	99.9	99.8
10	310	150	>99.9	99.9	>99.9	99.9

[a]Based on field analyses.

The organic condensates produced during the atmospheric pressure tests could easily be recycled as raw products to the refinery operation. This would reduce the actual operating costs of the TFE while removing organics from the wastes prior to disposal. The aqueous condensate was water saturated with the recovered organics and could be sent to existing wastewater treatment facilities at refineries. If the process is applied for the removal of volatiles only, the aqueous condensate could be recycled to the process feed, so that all water would exit with the process bottoms. (This would not be practical if large quantities of water were condensed, as in high-temperature operation).

The results from the pilot-scale land treatment apparatus tests showed that pretreating the waste with the TFE could reduce VO emissions by over 95 percent during land treatment compared to land treatment of the raw waste using typical land treatment practices. The tests also showed that the treated material biodegraded very well and that volatilization was minimal (1.1 wt.% and 1.6 wt.% of the applied oil during the month following waste application). At the end of the first month, heavy oil biodegradation continued at approximately the same rate. However, by that time all applied volatiles had either biodegraded or volatilized (6).

CONCLUSIONS

The thin-film evaporator used in this test was very effective at removing VO from the petroleum refinery sludges. Ninety-nine percent or more of the VO were removed under all operating conditions. Substantial amounts of some of the semivolatiles were also removed. The condensate from the atmospheric pressure runs separated cleanly into aqueous and organic phases. The organic condensate could be recycled and would therefore reduce the actual TFE operating costs. The aqueous condensate could be treated in existing wastewater treatment facilities. The bottoms from the TFE were still pumpable and land treatable. Air emissions from the pilot-scale land treatment of the treated waste were 95 percent less than from the land treatment of the untreated wastes.

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